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13. ABSTRACT (Maximum 200 words)

Specific goals: a) development of the versatile simulation tool to study morphology and transport in swollen polyelectrolyte membranes (PEM) of Nafion type at mesoscale (>20nm); b) understanding of the mechanisms of sorption and transport of chemical agents in swollen PEM.

We developed molecular models for Nafion and nerve agent simulant DMMP and explored microphase segregation and mechanisms of DMMP sorption and transport in hydrated membranes with K+ counterion. It was shown that in dry membranes DMMP partly dissolves in the polymer. However, in the excess of water, DMMP neither mixes with aqueous subphase nor dissolves within the polymer subphase; DMMP forms clusters at the interface. Via a series of molecular dynamics simulation, we parameterized a coarse-grained model of Nafion and performed a series of dissipative particle dynamics simulations of microphase segregation in hydrated membranes with different water content. With the increase of the water content we found a percolation-type transition at about 6 wt% from the system of isolated hydrophilic clusters to the three dimensional network of irregular channels forming a hydrophilic subphase. A random walk model was developed for DMMP diffusion in hydrated polymer including volume and surface mechanisms. Simulation results correlate with experimental studies at US Army RDECOM.

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FINAL PROGRESS REPORT

Molecular Modeling of Nafion Permselective Membranes

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Statement of the Problem

The search for novel polymeric membranes suitable as permselective diffusion barriers is one of the key problems in engineering new protective fabrics. These membranes must be impermeable to chemical and biological agents and, at the same time, provide high water vapor permeability, small heat accumulation, and reduced weight. It is anticipated that novel permselective membranes will be soon employed for protective clothing substituting currently available commercial materials such as the activated carbon loaded foam liner used in BDO. Two classes of permselective polyelectrolyte membranes (PEM) are currently considered as suitable candidates, which may provide desired protective, comfort, and mechanical properties: perfluorined membranes such as Nafion-type ionomers and sulfonated triblock copolymers of styrene and lower olefins. Unique sieving transport properties of permselective membranes are mostly determined by their complex heterogeneous microstructure and composition. A lack of understanding how the chemical composition of the polymer and solvent influences the nanostructure of PEM and how the membrane morphology affects the transport of water and chemical agents hinders guided design of novel protective fabrics.

In this project, we developed hierarchical molecular simulations tools to study the structural and transport properties of PEM with the example of Nafion. Hydrated Nafion membrane was studied on different scales from solvation of individual fragments and olygomers in water and organic solvents on atomistic level to mesoscale simulations of the segregation of the solvated membrane on nanometer scale to transport of chemical agents through membranes on micrometer scale. The results obtained on the atomistic level are employed on the mesoscale level and the morphologies obtained from the mesoscale simulations are employed for the macroscopic modeling. The main problem in simulations of Nafion is the absence of well-defined methods of mesoscale simulations of PEM, in particular, the incorporation of long-range electrostatic forces which are critical for systems like Nafion. The first practical approach to this problem was published in November 2003 [1]. To the best of our knowledge, the simulation of Nafion that we have performed is the first mesoscale simulation with explicit electrostatic forces included. The primary objectives of our research are as follows:

    (i)   development of simulation approaches to PEM

    (ii)   improving basic knowledge and understanding of the specifics of diffusive transport on the molecular level,

    (iii)   establishing correlations between chemical composition and molecular architecture and transport properties

    (iv)   development of rational models for predicting the membrane permeability/resistance with respect to water vapor and chemical agents

    (v)   correlation of the simulation results with ongoing experimental studies of Nafion membranes at US Army RDECOM

The selection of the systems targeted in our simulations was based on the parallel experimental studies of sorption and transport properties of Nafion membranes performed at RDECOM (Dr. Donald Rivin et al) [2] and SAXS and NMR studies of the structure of hydrated Nafion and water diffusion of Drs. Paul Inglefield and Alan Jones, Clark University [3]. The work was performed in coordination with experimental program of RDECOM, Natick, MA.

Summary of most important results

We have developed molecular level computational models of Nafion membrane microstructure and its transport/selectivity properties. The unique barrier properties of Nafion are primarily determined by its complex heterogeneous nanostructure. A solvated membrane undergoes nanoscale segregation into hydrophilic and hydrophobic subphases. By using Molecular Dynamics and Monte Carlo simulations we studied the membrane segregation at different degrees of solvation, ionic cluster formation, cooperative effects during solvation in mixtures (methanol/water), sorption of model chemicals such as dimethylmethylphosphonate (DMMP) in hydrated membranes, and mobilities of water, ions, and chemicals. We have found that while most phosphorus-based agents and their simulants are soluble in water, their solubility is hindered in hydrated Nafion membranes. DMMP concentrates at the interface between water and the organic fluorocarbon backbone. The hydration affects greatly the permeation of chemical agents. The mechanism of surface diffusion we discovered in simulations agrees very well with the experimental findings performed at RDECOM. A better understanding of chemical factors affecting the permeation/blocking mechanisms will facilitate the search for new protective materials. Our results are being used by RDECOM researchers in their studies of water solutions of nerve agent simulants and their permeation through membrane materials. Further, we have developed mesoscale simulation methods, particularly dissipative particle dynamics simulations, applicable to larger fragments of polymer membranes (>20nm). The model allows one to estimate the structural parameters (volume fraction or porosity, surface area, channel diameter) and the transport coefficients (permeability, conductivity) in the hydrophilic subphase. Also, it is possible to mimic SAXS, SANS, and NMR experiments to discriminate the structural models used for interpretation of the experimental data.

1. Atomistic level simulations of Nafion membrane.

In our earlier works [4-6], we developed an atomic level model of Nafion-1200 polymer and molecular dynamics (MD) simulation of Nafion solvation in water, methanol, and equimolar water–methanol mixture. The potential forcefield was based on electronic density calculations and simulations of vapor–liquid equilibrium of lower perfluoroalkanes and ethers, and thermodynamic properties of aqueous solutions of sodium sulfate. Typical conformations of Nafion olygomers in vacuum have been revealed. MD simulations of olygomers solvated in water and methanol revealed a noticeable difference between the geometries of the fluorocarbon skeleton in different solvents. The skeleton structure was substantially more folded in water than in methanol. The side chain of the Nafion olygomer was found to be quite stiff; only a few conformational transitions in the side chain were detected. Both water and methanol formed ca. 9 stable hydrogen bonds with the oxygens of SO_3^- group with the hydrogen bond lifetimes several times longer than rotational correlation times of individual solute molecules in the bulk. The other parts of the side chain were found to be hydrophobic; the ester oxy-gen closet to the side chain exhibited weak ability for hydrogen bonding to the solvent. The spatial distribution of solvent molecules, bonded to the SO_3^- group, was characterized by a pronounced anisotropic first solvation shell (Fig. 1).
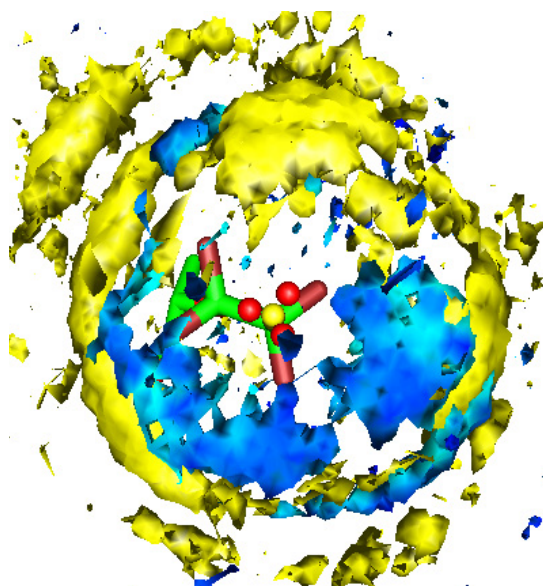
Fig. 1. Average coordinates of the atoms of the side chain in a reference coordinate system attached to S–O and S–C vectors and spatial distribution functions of the solvent oxygens around the side chain. The average local density of oxygens in gray regions is al least 2.2 times as large as the average number density of the solvent. Water in blue, methanol in yellow.
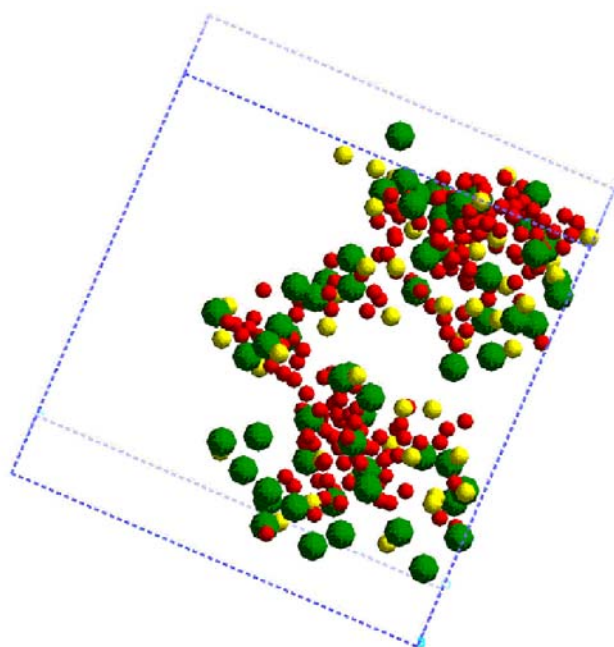

Fig. 2. Snapshot of large aqueous domains with surrounding SO_3^- groups and K^+ ions in system II. Water is shown in red, sulfur in yellow, potassium in green.

We performed MD simulation of hydration of Nafion membrane with K^+ as the counterion at different water content. Microphase segregation was observed in the system, developing with the increase of water content. Very good agreement with the experimental densities was obtained; reasonable agreement with experiment was also achieved for the diffusion coefficient of water and K^+ counterions. Water did not form a continuous subphase. Rather, we observed isolated domains containing less than 100 water molecules (Fig. 2). At high water content, the system of water domains gradually evolved. From our observations and comparison of the predicted diffusion coefficients with the experimental values, it follows that it is not necessary to assume the hydrophilic phase to be continuous in order to yield the diffusion coefficient as high as experimentally observed. Presumably, the connections between hydrophilic clusters dynamically open and close, providing on average a nonzero conductance at low water uptake.

The results obtained on the atomistic level are instructive and shed light on the specifics of membrane microsegregation and transport, but the size of the basic cell and the total length of the simulations (1.5ns) are not sufficient to draw decisive conclusions about the morphology of microphase segregation and the mechanisms of water transport in swollen Nafion membranes. However, they constitute the basis for the development of mesoscale simulation methods.

2. Simulation of interaction of dimethylmethylphosphonate (DMMP) with Nafion membrane.

We have explored the mechanisms of sorption and diffusion of DMMP [Vishnyakov, 2004 #75] in dry and hydrated Nafion membranes. It should be taken into account, that no forcefields for alkylphosphonates have been suggested in the literature so far. Thus, we first developed a united-atom

second-order potential model for DMMP designed to reproduce molecular conformations and physical properties, such as the liquid density, heat of evaporation and thermal expansion coefficient of the pure liquid. Using the model, we explore molecular structure, thermodynamic characteristics, and dynamic properties of liquid DMMP and its aqueous solutions by molecular dynamics (MD) simulations. We obtained very reasonable agreement with the limited experimental data on aqueous solutions of DMMP. It was shown that in average, one DMMP molecule forms two hydrogen bonds with surrounding water via the oxygen atom that forms a double bond to phosphorus. No long-living DMMP·H2O complexes in the aqueous solutions were found. The model of DMMP can be used in simulations of actual phosphorous nerve agents.
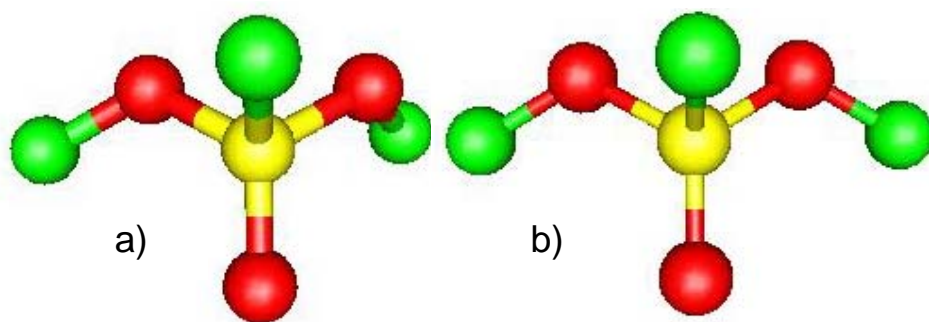

Figure 3. Two main conformations of DMMP predicted by the model. These conformations agree with ab-initio [7] studies and indirect experimental observations [8]. The parameters of the forcefield were published in ref [9]

In conjunction with experimental studies at RDECOM, our simulations revealed the mechanisms of sorption and transport of DMMP in hydrated Nafion membranes [Rivin, 2004 #76]. In particular, our MD simulation of water/DMMP interactions with Nafion provides an insight into how competitive solvents effect solubility and transport behavior in the phase segregated ionomer. Simulations were conducted for a thin film model formed from six oligomers consisting of four repeat units of the potassium sulfonate terminated fluoroether side chain with associated fluorocarbon backbone. In the absence of water, DMMP dissolves almost completely in the fluoroether phase. DMMP does not solvate the free cation but causes association of $-SO_3^- K^+$ end groups. Water is concentrated exclusively in the ionic regions and does not mix with the fluoroether phase. Water causes ionization of the potassium sulfonate salt and forms ionic channels at the interface with the fluoroether side chains. In the mixed solvent system, containing excess water, redistribution of DMMP occurs. At the low DMMP concentration treated in the molecular modeling, over 70% of DMMP is located at the interface of the side chain phase in contact with water and more than 20% is dissolved in water, with less than 4% dissolved in the interior of the fluoroether phase.

The molecular modeling provides a basis for understanding the effect of DMMP water interactions on the permeation behavior. In the absence of water, DMMP transport occurs exclusively within dispersed fluoroether regions governed by side chain mobility, with long range transport determined primarily by tortuosity. In the mixed solvent, DMMP redistribution to the hydrophilic interface and solution in the aqueous phase causes enhanced DMMP transport in co-current flow via water solvated ionic pathways and solution in the more mobile aqueous environment. In counter current flow, the benefits associated with the water are offset by the opposing concentration gradients, water concentration is smallest where DMMP concentration is highest, and the opposing direction of the flows. Water transport occurs solely in an aqueous phase surrounding hydrated sulfonate end groups. The reduction of water flux by DMMP can be attributed to the association of water with DMMP at the fluoroether interface and a decrease in the fraction of free water in the aqueous solution. It is likely that the polar, water containing channels are narrowed by intrusion of DMMP at the interface and by extensive swelling of the fluoroether phase at high concentrations of DMMP.

Although the present modeling is developed under conditions of dilute DMMP and high water concentrations, some of the conclusions of the single solvent and mixed solvent systems can be extended to higher DMMP concentrations and other counterions [10].
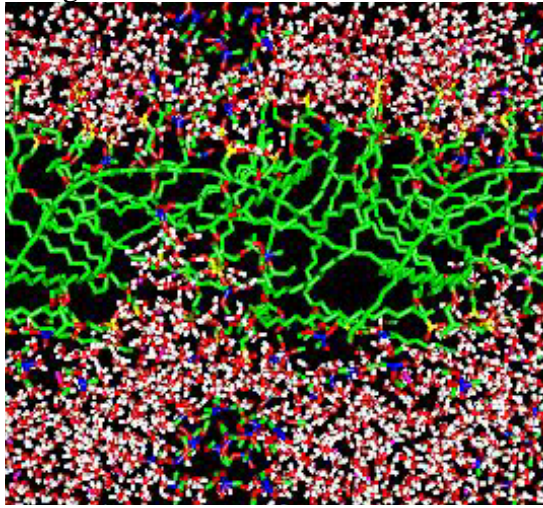
C in green

O in red

H in white

P in blue

S in orange

K in pink

Figure 4. Shapshot of Nafion polymer layer solvated in water-DMMP mixture. The presence of Nafion limits the solubility of DMMP in water. DMMP concentrates on the surface of polymer rather than is dissolved in water

3. Development of the mesoscale simulation models of PEM.

In the mesoscale simulations of Nafion membrane, we applied dissipative particle dynamics (DPD) method simulations, Nafion was presented as a sequence of beads:

```
CCCCCCCCCCCC . . . .
   S      S
```
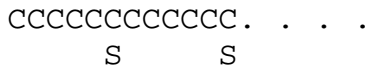
Fig. 5 Schematic model of Nafion polymer: C -skeleton beads, S – sidechain beads

where C denotes a part of skeleton, and S denotes the sidechain. In DPD, the interactions between the beads are short-ranged and purely repulsive, and the beads where connected by harmonic springs with. There were two types of water beads: (i) pure water (ii) water with K+ counterions inside. Water beads were not connected by bonds. Because of the limited size of the sidechain, size of the bead for the skeleton and water is also limited. In this work, we assumed 1 bead = 6 CF2 groups, which corresponds to the bead diameter σ = 0.76nm. We used three sets of input data to fit the parameters repulsive interactions: (i) experimental PVT data of Nafion and water (ii) radial distribution functions for fluorocarbons in water obtained in atomistic MD simulations.

The main problem in mesoscale simulations is accounting for the ionic interactions. Electrostatic charges were "smeared out" over the effective spherical bead and the electrostatic forces were calculated as derived in ref [1]. At large distances the interactions of charged spheres are identical to the interaction between two point charges. Ewald summation was applied in order to account for long-range electrostatic interactions. We performed DPD simulations in a cubic system of 21.2nm in length (28*28*28σ). The total number of beads was 67,000 and the total simulation length about 1μs. We started from a random configuration, where a static minimization was first performed, and finished the simulation when the energy was stabilized. Although it is unclear whether the true equilibrium was reached in the system, no progress to an ordered state was observed in the simulations.

We performed three simulations with the water content of 3, 6, 12, and 17 wt %. 12% wt approximately corresponds to the saturation. At the water content of 3 wt%, all three systems, we observed formation of separated hydrophilic clusters, containing water and sidechains, of about 1.5nm in diameter. At higher water contents, a continuous hydrophilic subphase was formed. We did not observe any particular segregation morphology in any of the systems. However, the tessellation analysis shows that the

hydrophilic subphase is comprised of a three dimensional network of irregular channels of the average diameter of 2, 2.5 and 3 nm at 6, 12 and 17 wt% of water, respectively.
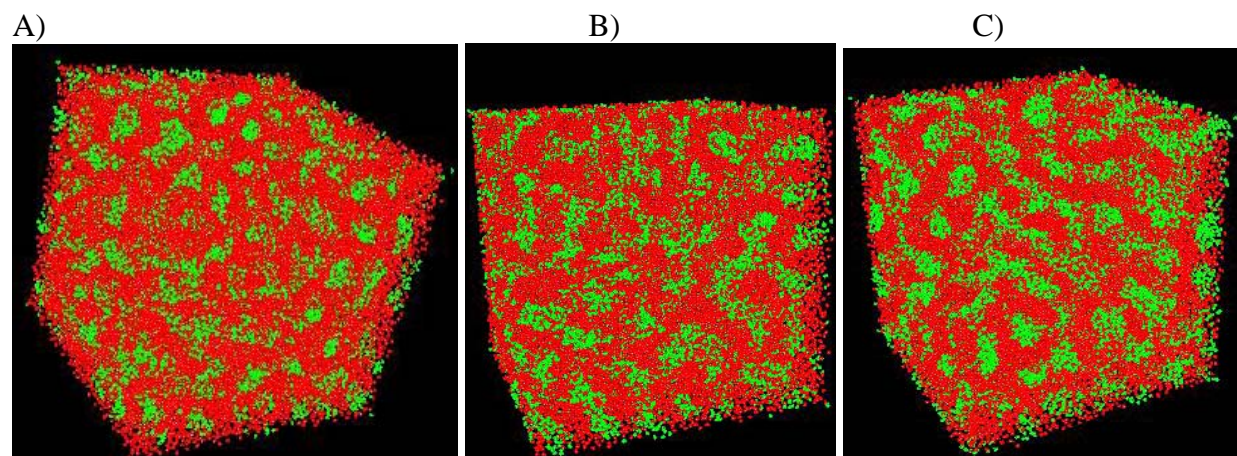
A)   B)   C)

Figure 6. Final snapshots of the microsegregation in hydrated Nafion membranes at 6 (a), 12 (b) and 17 (c) wt % of water. Hydrophilic phased in green (water,sidechains, counterions), hydrophobic subphase in red

To conclude, we have developed a versatile simulation tool to generate mesoscopic fragments of solvated Nafion membranes. The structural model shows with the increase of the water content a percolation-type transition from the system of isolated hydrophilic clusters to the three dimensional network of irregular channels forming a hydrophilic subphase. We have developed a model (and a program) for DMMP diffusion in hydrated polymer that includes both volume and surface mechanism, however the utilization of this model for practical calculations is hindered due to the lack of experimental data on surface diffusion of DMMP. We will continue to collaborate with US Army RDECOM to exploit the model for analyses of experimental studies and recommendations on the use of Nafion-type membranes for protective clothing. The DPD simulation tool developed for Nafion will be used in our ongoing project W911NF-04-0239 for simulation of phase segregation in sulfonated triblock copolymer permselective membranes.

Listing of Publications and Technical reports

A) Publications in peer-reviewed journals

D. Rivin, G. Meermeier, N.S. Schneider, A. Vishnyakov and A. V. Neimark, - **Simultaneous Transport of Water and Organic Molecules through Polyelectrolyte Membranes**, Journal of Physical Chemistry B, 2004, V.108, p.p. 8900-8909.

A. Vishnyakov and A. V. Neimark, - **Molecular model of dimethyl -methyl- phosphonate and its interactions with water**, Journal of Physical Chemistry A, 2004, V.108, p.p. 1435-1439.

B) Publications in conference proceedings

A. Vishnyakov and A. V. Neimark **Interactions of dimethyl methyl phosphonate with hydrated Nafion membranes** AICHE Annual Meeting 2003, paper 80E

C) Papers presented at conferences, but not published

A. Vishnyakov and A. V. Neimark **Molecular modeling of microstructure and water sorption and transfer in permselective nafion membranes**. AICHE Annual Meeting, Los Angeles, Nov 2001. Paper 112f.

A. V. Neimark, A. Vishnyakov **Molecular Simulation of Phase Separation and Transport in Nafion Membranes.** Invited Paper. Computational Chemistry Symposium. 203rd Electrochemical Society Meeting Paris, France, April 27-May 2, 2003.

D) Technical reports submitted to ARO and US Army RDECOM

Report 1. Molecular model for dimethyl methyl phosphonate
Report 2. Simplified model for nafion skeleton and sidechain. Optimization of the sidechain.
Report 3. MD simulations of pure dimethyl methyl phosphonate
Report 4. MD simulations of DMMP-water mixtures.
Report 5. MD simulations of DMMP and dmmp-water mixture in presence of model nafion sidechains.
Report 6. MD simulations of water, dmmp and dmmp-water mixture in a contact with nafion polymer film.
Report 7. Influence of counterion charge on solvation of Nafion membraned by water and DMMP
Report 8. Mesoscale simulations of Nafion membranes

Participating Personnel

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Dr. Aleksey Vishnyakov, staff scientist

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(10)   RIVIN D.; MEERMEIER G.; SCHNEIDER N.; VISHNYAKOV A.; NEIMARK A. V. Simultaneous Transport of Water and Organic Molecules through Polyelectrolyte Membranes *J. Phys. Chem. B* **2004**, *108*, 8900.